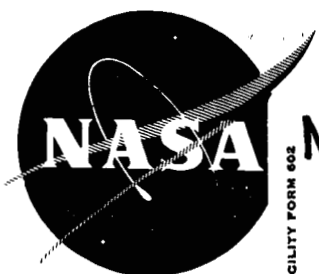


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RESEARCH & DEVELOPMENT OF A HIGH CAPACITY NONAQUEOUS SECONDARY BATTERY

FOURTH QUARTERLY REPORT

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NASA
Lewis Research Center
Auxiliary Power Generation Office
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I. INTRODUCTION

Basic electrochemical experiments serve to demonstrate the utility of various electrode systems for incorporation in secondary batteries. Since the performance of an electrode is dependent on the electrolyte in which it operates, it is extremely important that a clear correlation between experimental electrochemical data and electrolyte composition be realizable. With the establishment of such correlations one may proceed in a logical and systematic fashion towards modifying electrolyte composition to improve electrode performance.

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During this quarter our principal concern has been to establish more clearly the relationship between known variations in electrolyte composition and observed changes in electrode behavior. A good deal of emphasis has been given to studying the effects resulting from the deliberate addition of water to various propylene carbonate solutions. We have not only been concerned with the role water may play as a deleterious and difficultly removable impurity but also as an excellent Lewis base by which the electrolyte composition may be modified and studied in a systematic fashion.

Author

In determining the magnitude and causes of polarization there are important differences in the study and interpretation of electrochemical data obtained in non-aqueous as opposed to aqueous systems. It is therefore not possible to interpret the results of single experiments performed over a small range of experimental conditions by simple analogy to aqueous systems. Rather, it is necessary to perform a variety of electrochemical experiments over a wide range of conditions in order to establish broad, general patterns of behavior within which detailed analysis may proceed more efficiently, and this work has continued.

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II. EXPERIMENTAL APPARATUS

Electrochemical experiments have been conducted in cells similar to that shown in Figure 1. The counter electrode chamber on the left is connected to the working electrode chamber through a fine glass frit. The cell is stoppered with a Teflon cover. Argon is constantly supplied either through the glass bubbler or over the surface of the solution. The working electrode is shown in greater detail in Figure 2. The silver disc in the center of the epoxy filled glass cylinder serves as the reference electrode, while the outer discs may consecutively serve as working electrodes. Experiments involving the evolution of HCl, pages 22-25, were conducted in 250 ml. Erlenmeyer flasks. A single electrode of the type shown in Figure 2 was inserted through a rubber stopper, one disc serving as the working electrode, a second as the counter electrode, and a third as reference electrode. It will be noted that the total amount of electrolysis conducted during these experiments produces but negligible changes in electrolyte composition. In all experiments the electrodes were routinely polished with 0.3 micron alumina prior to insertion in the cell. This was found necessary in order to insure reproducible results.

Constant current was supplied through electronically regulated, fast response instruments. Potentiostatic measurements were performed with a Wenking potentiostat. The potential of the working electrode with respect to the reference electrode was measured with a high-impedance electrometer, the output of which drove a strip-chart potentiometric recorder.

The propylene carbonate solvent was purified by vacuum distillation at 77°C and 2 mm. Hg through a 90 cm. vacuum jacketed column packed with Berl saddles. Distillate is discarded until the above temperature and pressure is obtained at a reflux ratio of 1 to 1. Karl Fisher titration indicates the solvent so obtained contained about 0.02% in water. Further purification of the salts from which the electrolytes were prepared was not attempted by us. The solutions were prepared by weighing requisite amount of salt in a dry box and adding the material to the requisite amount of purified solvent.

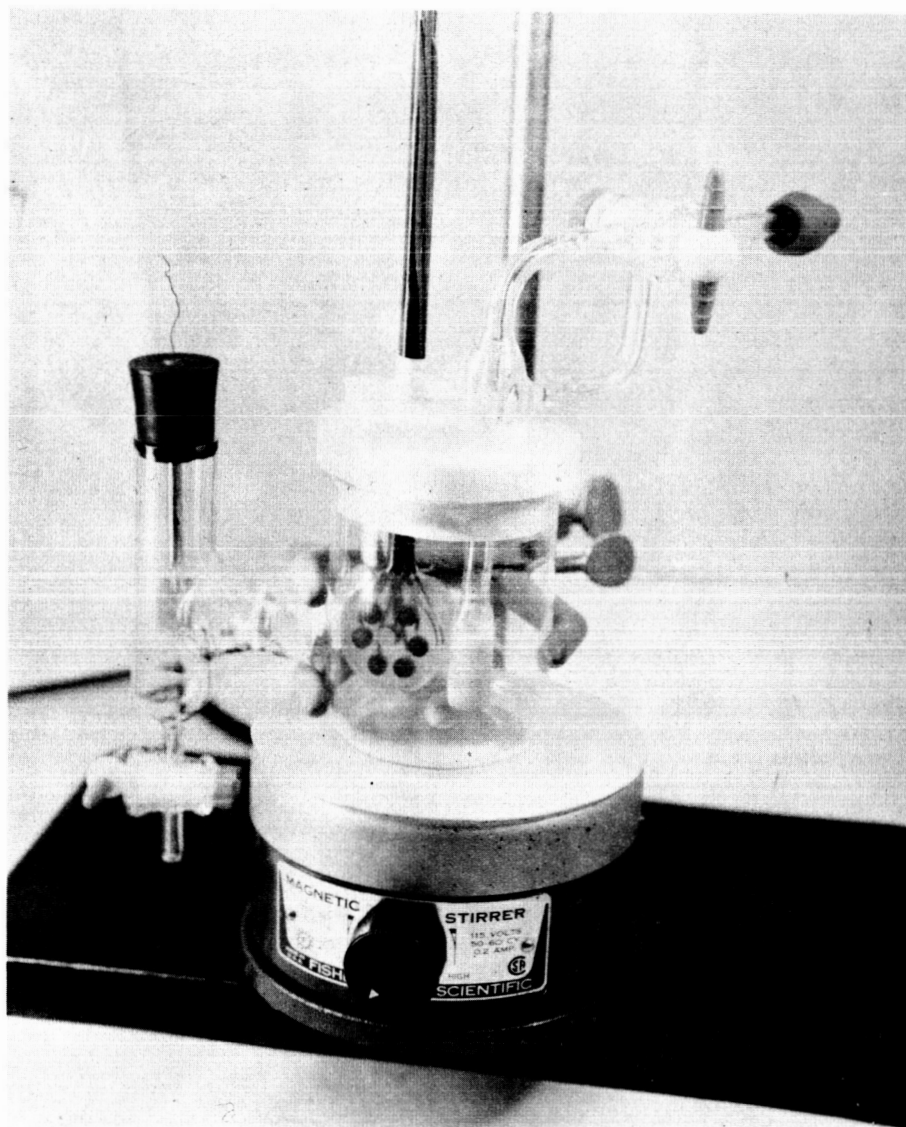


Figure 1: Electrolysis cell for the performance of electrochemical experiments, showing counter electrode chamber on left and working electrode chamber on right in which are immersed electrode and deaeration apparatus.

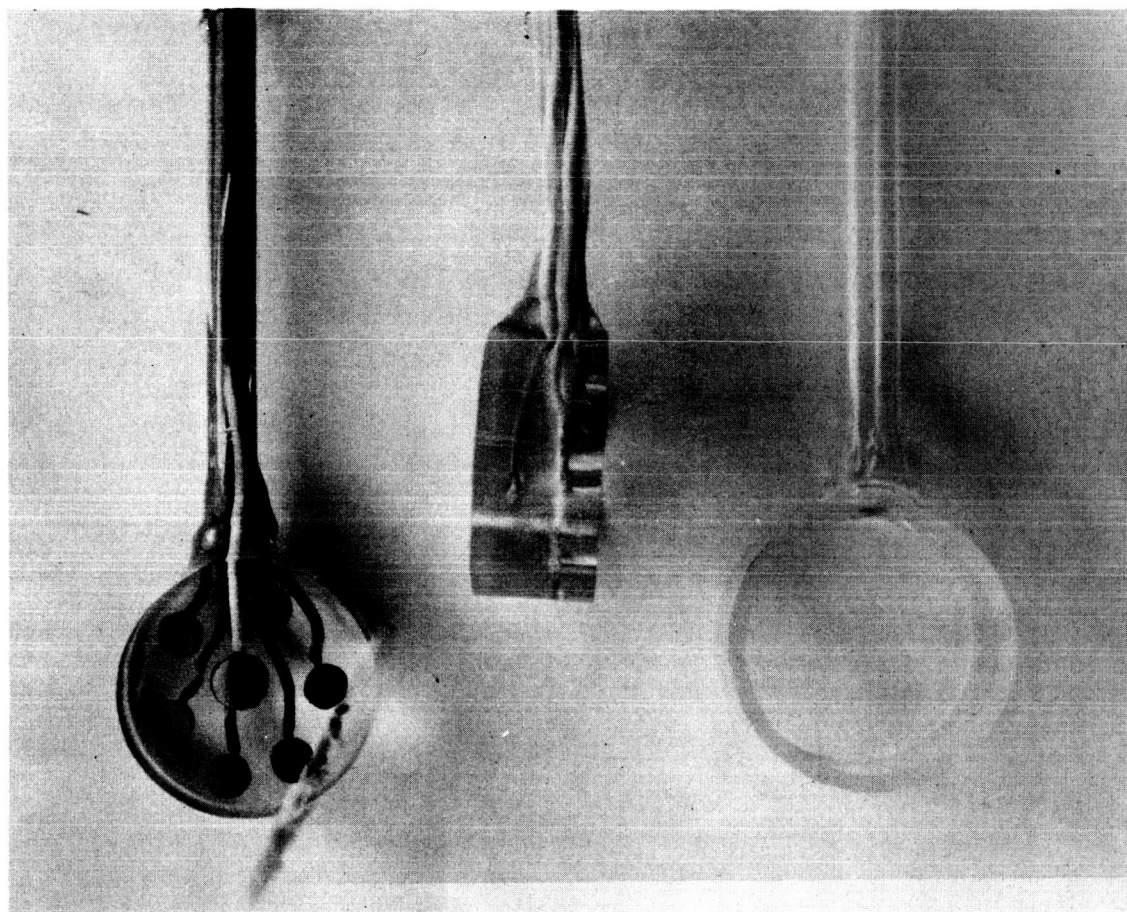


Figure 2: Electrode, shown approximately actual size. On the right is shown the glass structure from which the electrode is prepared. Metal discs sliced from high purity metal rod are soldered to individual insulated copper wires. The discs are sealed in epoxy resin and the surface is polished. Front and side views of a completed electrode are shown in the left and center. Normally the circumferential discs serve as individual working electrodes and the center disc, of silver, serves as the reference electrode without further treatment.

III. THE LITHIUM ELECTRODE

A. Summary of Previously Reported Work

The failure to obtain satisfactory anodic efficiency in the electrolytic re-oxidation of lithium deposits was ascribed to phenomena occurring during the cathodic portion of the cycle, wherein it appeared both lithium metal and lithium oxide or hydroxide co-deposited. It has also been shown that there is normally present in propylene carbonate electrolytes significant concentrations of electroactive material reducible at potentials more noble than that at which lithium is deposited and this material is hereafter denoted "species A". Some improvement in behavior can be obtained by pre-electrolysis whereby a large portion of this material is removed. A procedure for preparing AlCl_3 electrolytes containing smaller concentrations of this undesirable material was developed and reported in the Third Quarterly Report, page 17. The presence of water had been reported⁽¹⁾ to be deleterious but preliminary experiments indicated that the deliberate addition of water did not result in predicted phenomena such as hydrogen evolution at low currents or the chemical removal of deposited lithium.

B. Subsequent Observations and Conclusions

During the fourth quarter experiments on the lithium electrode have been directed toward obtaining a clearer picture of the effects produced by the deliberate addition of water, and a further assessment of the role played by Species A and the possibility of obtaining complete removal of this material. Attempts to modify and improve the performance of the lithium electrode by varying the nature of the solute contained in the electrolyte from which lithium was electrodeposited have been unsuccessful in significantly increasing anodic efficiency, and have made it clear that further analysis of the behavior of this electrode must await more detailed knowledge of the composition of the electrolyte.

1. Effect of water on the behavior of the lithium electrode.

Experiments were performed in which water was deliberately added to a solution of lithium perchlorate and the effect of water assessed by an examination of the chronopotentiometry for lithium reduction, and by electrochemical and chemical analysis of the resultant deposits. A propylene carbonate

(1) Lockheed Missiles and Space Co., Palo Alto, California, Quarterly Report 2, Contract AF 33(616)- 7957, April 1963.

solution, 0.2 M in LiClO_4 was prepared. The cathodic chronopotentiometry was first performed, and well-defined chronopotentiograms were obtained, which became progressively less well-defined with increasing amounts of water. In Figure 3 are shown typical chronopotentiograms obtained before the addition of water (solid line) and after adding water to a final concentration of 0.42 M (dotted line). Subsequent to the cathodic chronopotentiometry depositions were performed in stirred solution at 5 mA cm^{-2} for 30 seconds, followed by immediate reversal of the current. The current density used was arbitrarily selected within a range dictated by the fact that very short transition times cannot be read on the recorder while at transition times longer than 40 to 50 seconds convection begins to occur at the electrode surface. Completion of anodization was marked by a sharp rise in potential, and anodic efficiencies were calculated by dividing the time required for completion of anodization by the time allowed for cathodization, 30 seconds (see page 11). The results are reported below:

Concentrations of water added in moles liter ⁻¹	$iT^{1/2}$ in $\text{mA cm}^{-2} \text{ sec}^{1/2}$	Anodic efficiency
0	35	50%
0.01	33	45%
0.02	--	43%
0.04	35	42%
0.08	33	32%
0.12	33	33%
0.22	*	27%
0.32	*	22%
0.42	*	18%
0.51	*	8%
0.61	*	5%
0.86	**	negligible

* At concentrations of water greater than 0.22 M, the cathodic chronopotentiograms were so ill-defined as to preclude reasonable determination of $iT^{1/2}$.

** Cathodic chronopotentiograms exhibited a preliminary potential plateau at about -1.5 V, but $iT^{1/2}$ was quite irreproducible.

If the reaction, $\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + \text{O}^{--}$, were to occur, and if the mobility of water in these electrolytes were comparable to that of lithium ion, one would expect a limiting current for water reduction in stirred solution of about 100 mA cm^{-2} multiplied by the concentration of water. Thus a limiting current of 5 mA cm^{-2} would be expected when the

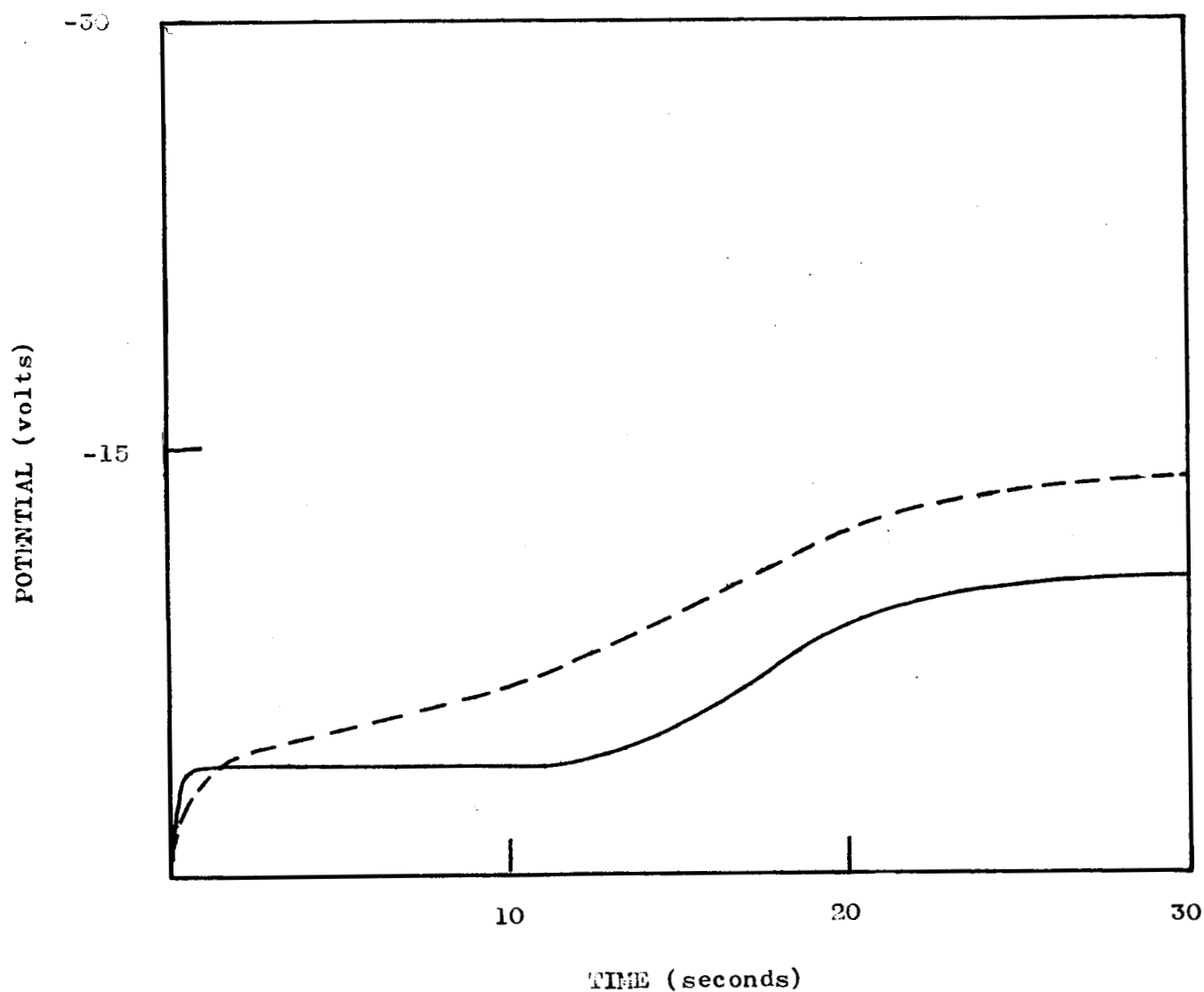


Figure 3: Cathodic chronopotentiometry in 0.2 M LiClO_4 . Chronopotentiograms performed on polished copper electrodes at 9 mA cm^{-2} . Solid line represents chronopotentiogram obtained prior to addition of water; dotted line represents chronopotentiogram obtained after solution made 0.42 M in water.

concentration of water was only 0.05 M.⁽²⁾ The results of our experiments indicate that water is not reduced independently of and prior to the reduction of lithium, and the fact that a potential plateau is observed at values lower than the lithium deposition potential only when the concentration of added water is more than four times the concentration of lithium initially present suggest that the complexation of water with lithium ions occurs, and that the water so complexed is not reduceable independently of the reduction of lithium.

Further experiments were performed in propylene carbonate, 0.2 M in LiClO_4 , in which prolonged depositions were conducted following each addition of water and the deposits were chemically analyzed. The limiting current for the reduction of lithium in solutions of this concentration is about 20 mA cm^{-2} in stirred solution. Depositions were conducted at currents considerably larger than this value, at 60, 120, and 180 mA cm^{-2} , for a period of time giving a total of 15,000 millicoulombs cm^{-2} of cathodization at each current density. After deposition, the electrodes were immersed in water and the amount of base released was titrated with standard acid. Vigorous gassing occurred during deposition, and the potential of the electrode increased linearly with time. In Figure 4 is shown a typical recording of potential versus time. Following the final addition of water the total concentration of water was 0.8 M; nevertheless, in all cases it was observed that the equivalents of base produced by cathodic electrolysis were exactly equal to the total equivalents of current passed.

The above results suggest that reactions of the following type may occur during cathodization:

(2) It is normally true that, in agitated solution, the limiting current is proportional to the concentration of electroactive material in solution (J. J. Lingane, Electroanalytical Chemistry, Interscience Publishers, Inc., New York, 1958, pp. 200, 224.) however, the proportionality constant can be theoretically derived only under very particular conditions and resort must be made to an empirical evaluation of this constant. The product, $i_T^{1/2}$, can be theoretically derived and is related to the concentration of electroactive material by the Sand equation:

$$i_T^{1/2} = \frac{\pi^{1/2} n F A D^{1/2} C}{2}$$

(See, e.g., op. cit., p. 620). In propylene carbonate solution we find that the empirical observed limiting current in mA cm^{-2} is about half the value for $i_T^{1/2}$ in $\text{mA cm}^{-2} \text{ sec}^{1/2}$.

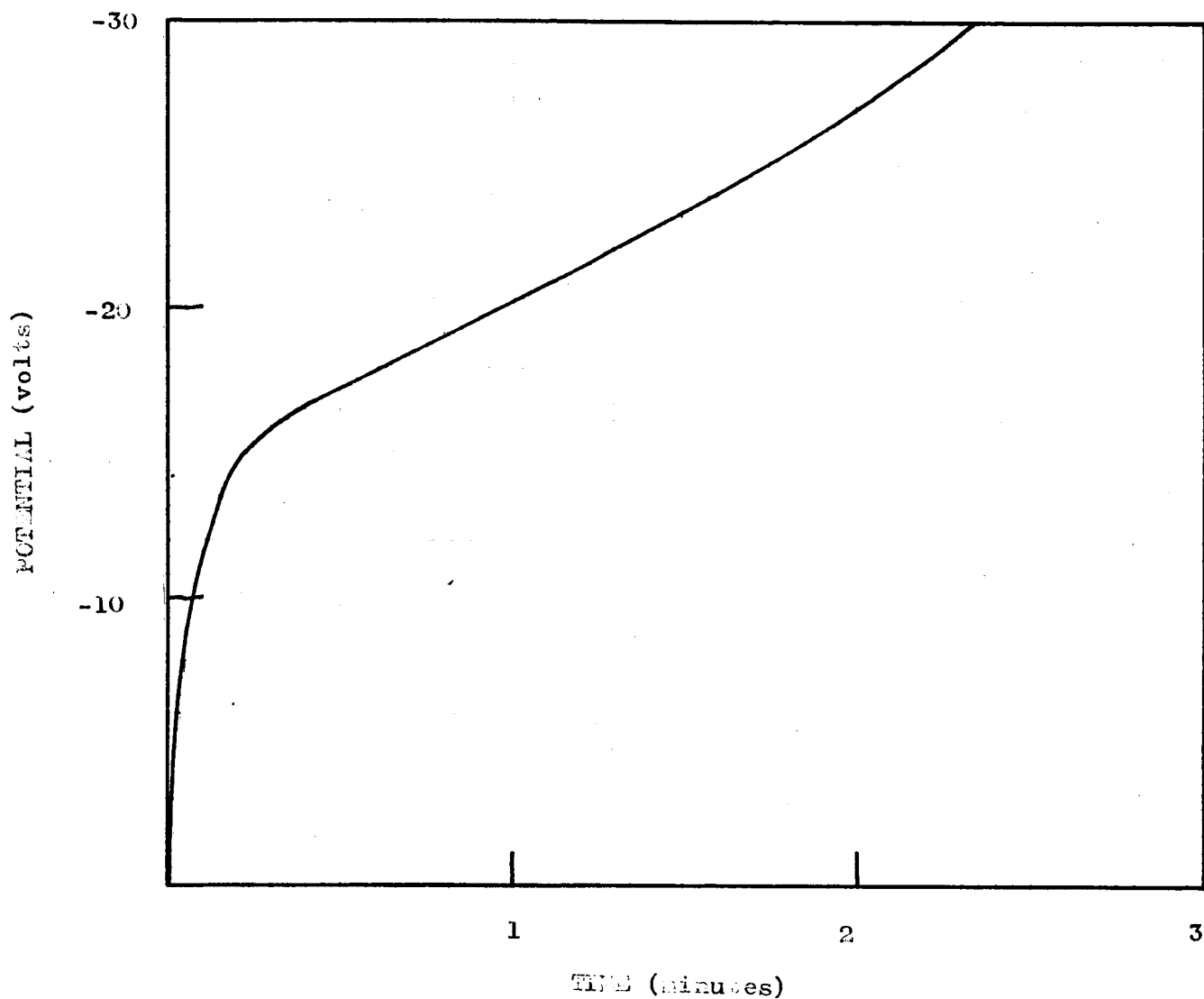
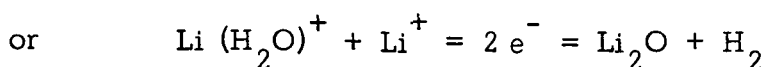
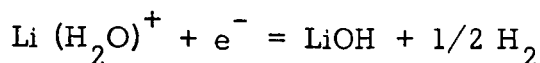


Figure 4: Cathodic chronopotentiogram obtained in a solution initially 0.2 M in LiClO_4 and 0.66 M in water. Chronopotentiogram obtained on polished copper₄ electrode at 60 mA cm^{-2} .



The pH titration curves obtained were identical to those displayed when an equivalent amount of strong alkali was titrated with standard acid. This indicates that the deposit is a strong base and not, for example, Li_2CO_3 .

The linear increase in potential observed on prolonged cathodization is that expected if the deposit is poorly conductive, and is identical to the type of phenomena observed when a valve metal such as aluminum or tantalum is anodically oxidized in an appropriate electrolyte. From the rate at which potential increases as shown in Figure 4, and assuming that the deposit is Li_2O with the same density as crystalline lithium oxide, 2.01 g cm^{-3} , one can calculate the resistivity of the basic film

from the equation: $R = \frac{r l}{A}$, where R is the resistance, r the resistivity, l the thickness of the film, and A the electrode area. Since $R = V/i$ then $V/i = r l/A$. Taking the derivative with respect to time and rearranging one obtains $dV/dt = (ri/A) dl/dt$ where dV/dt is the slope of the experimental curve in Figure 4 and dl/dt is the rate of film growth. Assuming that the film is Li_2O with the same density as the crystalline salt one calculates that the rate of increase of film thickness is $4.5 \times 10^{-3} \text{ cm sec}^{-1}$. The rate at which the resistance increases is $0.92 \text{ ohm sec}^{-1}$. The resistivity therefore is:

$$r (\text{ohm-cm}) = \frac{(0.92 \text{ ohm sec}^{-1}) (1 \text{ cm}^2)}{(4.5 \times 10^{-3} \text{ cm sec}^{-1})} = 200,000 \text{ ohm-cm}$$

Since the addition of water in substantial amounts appears to result in the co-deposition of lithium oxide or hydroxide, which is undesirable, it may be expected that better performance would be obtained following the addition of material expected to more strongly bind the water than does the lithium ion. Since AlCl_3 is expected to behave in this fashion, experiments were performed in which water was added to solutions of LiCl and AlCl_3 and the anodic recovery measured. A solution of propylene carbonate, 0.35 M in LiCl and 0.4 M in AlCl_3 , was investigated for this purpose. The limiting current for lithium reduction in such a solution is about 35 mA cm^{-2} in stirred solution, and cathodizations were conducted at 20 mA cm^{-2} . Electrolyses were performed in stirred solution for 20 seconds, followed by immediate reversal of the current to determine anodic efficiency. A more careful examination of the presence of species A was made by cathodic chronopotentiometry since the presence of species A is evidenced

by fairly well-defined chronopotentiograms with a potential plateau at about -1 Volt followed by a moderately sharp rise to the lithium deposition potential of about -3V. (3) In the following presentation of the results, $iT^{1/2}$, for this initial break is given. Recalling that the limiting current for a process is, in mA cm^{-2} , about half the value of $iT^{1/2}$, one can see that the decrease in anodic recovery cannot be due to concurrent reduction of this material:

<u>Concentration of water in moles liter⁻¹</u>	<u>$iT^{1/2}$ in $\text{mA cm}^{-2} \text{ sec}^{1/2}$</u>	<u>Anodic efficiency</u>
0	5.0	68%
0.05	5.0	50%
0.1	5.7	50%
0.15	6.3	40%
0.25	6.8	28%
0.35	7.2	26%
0.50	7.6	23%
0.65	8.3	21%
0.8	9.0	21%
1.0	9.3	negligible

Since it would be expected that any water should chemically attack metallic lithium, experiments were performed in which the rate at which lithium was oxidized chemically was measured, and it was found that the effective rate of lithium dissolution by chemical reaction was only about 2 mA cm^{-2} . The experimental procedures used are outlined in the Second Quarterly Report.

A comparison of the results obtained on the addition of water to solutions with and without AlCl_3 indicates that no significant improvement in performance was obtained.

(3) It should be noted that the presence of species A in solutions in which AlCl_3 is absent is not easily detected by cathodic chronopotentiometry since the chronopotentiograms are so ill-defined; thus we have not made similar studies in solutions of LiClO_4 and KPF_6 alone.

2. Further experiments on the variation of anodic efficiency with conditions of deposition. The results shown on pages 6 and 11 suggest that some improvement in anodic efficiency is obtained when AlCl_3 is present in solutions with low water concentration. Further experiments were performed in which an attempt was made to determine whether any clear correlation between anodic efficiency and the concentration of AlCl_3 could be established. Such experiments involved the addition of small increments of AlCl_3 to a solution of LiClO_4 followed by measurement of the anodic efficiency as a function of current density and total current of cathodization. These experiments were unsuccessful in that the variations of anodic efficiency obtained within an experiment were larger than any variation observed as a result of increasing the concentration of AlCl_3 and no clear correlation could be established. At present we can only say that AlCl_3 appears to produce but marginal improvement in anodic efficiency.

The anodic efficiency is diminished if the electrode is not thoroughly cleaned after each run. Typical results were obtained when first propylene carbonate solution, 0.2 M in LiClO_4 , was cathodized at 25 mA cm^{-2} for 120 seconds on polished copper, followed by immediate current reversal. After completion of anodization cathodization was again performed under the same conditions. Successive anodic efficiencies of 48.5%, 7.5%, and 2.0% were obtained. When electrolysis was continued for only 40 seconds for each cathodization, successive anodic efficiencies of 54.8%, 44.7%, 15% and 7% were obtained.

Again it must be emphasized that anodic efficiency does not appear to be a function of the conditions of anodization. If a series of cathodizations are performed under identical conditions followed by subsequent anodization at various currents, or potentiostatically over a range of potentials, significant variations in anodic efficiency are not obtained. This seems to indicate that poor anodic efficiency due to passivation or to destruction of electrical contact does not occur.

3. Further experiments on the detection and removal of species A. We have previously reported in the Second Quarterly Progress Report on page 9 that one of the difficulties in the detection and removal of species A lies in the fact that electrolytic reduction of this material appears to result in the deactivation of the electrode. Our main objective in obtaining complete removal of this material is the desire to examine the behavior of the lithium electrode at very low currents. To date this cannot be done since, at low currents, most of the current will be used in reduction of species A rather than of lithium.

A solution of propylene carbonate, 1.0 M in LiClO_4 and 0.1 M in AlCl_3 , was prepared. Cathodic chronopotentiograms were obtained. A typical chronopotentiogram is shown in Figure 5. Three potential breaks are observed prior to lithium reduction, and the value for $iT^{1/2}$ reported for species A is that calculated from the last potential break. A solution, 0.35 M in LiCl and 0.4 M in AlCl_3 , was similarly studied and a typical cathodic chronopotentiogram is shown by the dotted line in Figure 5. The differences in the chronopotentiograms further suggest that species A in fact comprises several substances, the relative proportions of which vary from electrolyte to electrolyte.

To further demonstrate the improvement obtained on removal of species A anodic efficiencies were determined for lithium in the $\text{LiCl}/\text{AlCl}_3$ solution described above. Cathodizations were conducted in stirred solution at the current indicated below for 20 seconds, followed by immediate current reversal. The solution was then electrolyzed potentiostatically overnight following which $iT^{1/2}$ for species A had diminished from about $7.5 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ to $3.4 \text{ mA cm}^{-2} \text{ sec}^{1/2}$. Anodic efficiencies were again determined under the same conditions as described above.

<u>Current density in mA cm^{-2}</u>	<u>Anodic efficiency with- out pre-electrolysis</u>	<u>Anodic efficiency after pre-electrolysis</u>
1.25	--	5%
5	--	40%
10	--	50%
15	25%	65%
20	27%	68%
25	40%	70%
30	50%	73%
35	50%	78%
40	40%	--

The same solution was again electrolyzed overnight but no further improvement was observed either in a diminishment of $iT^{1/2}$ for species A nor in an increased anodic efficiency. Thus ultimate limitations appear to exist to the pre-purification possible by pre-electrolysis. It should be noted that a value for $iT^{1/2}$ of $7.5 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ corresponds to a concentration of species A of 0.037 N which is much too large to be ascribed to the presence of impurities in the AlCl_3 , LiCl , or LiClO_4 , from which the electrolytes have been prepared.

4. Experiments in KPF_6 electrolytes. A solution of propylene carbonate, 0.2 M in KPF_6 , was investigated by cathodic chronopotentiometry.

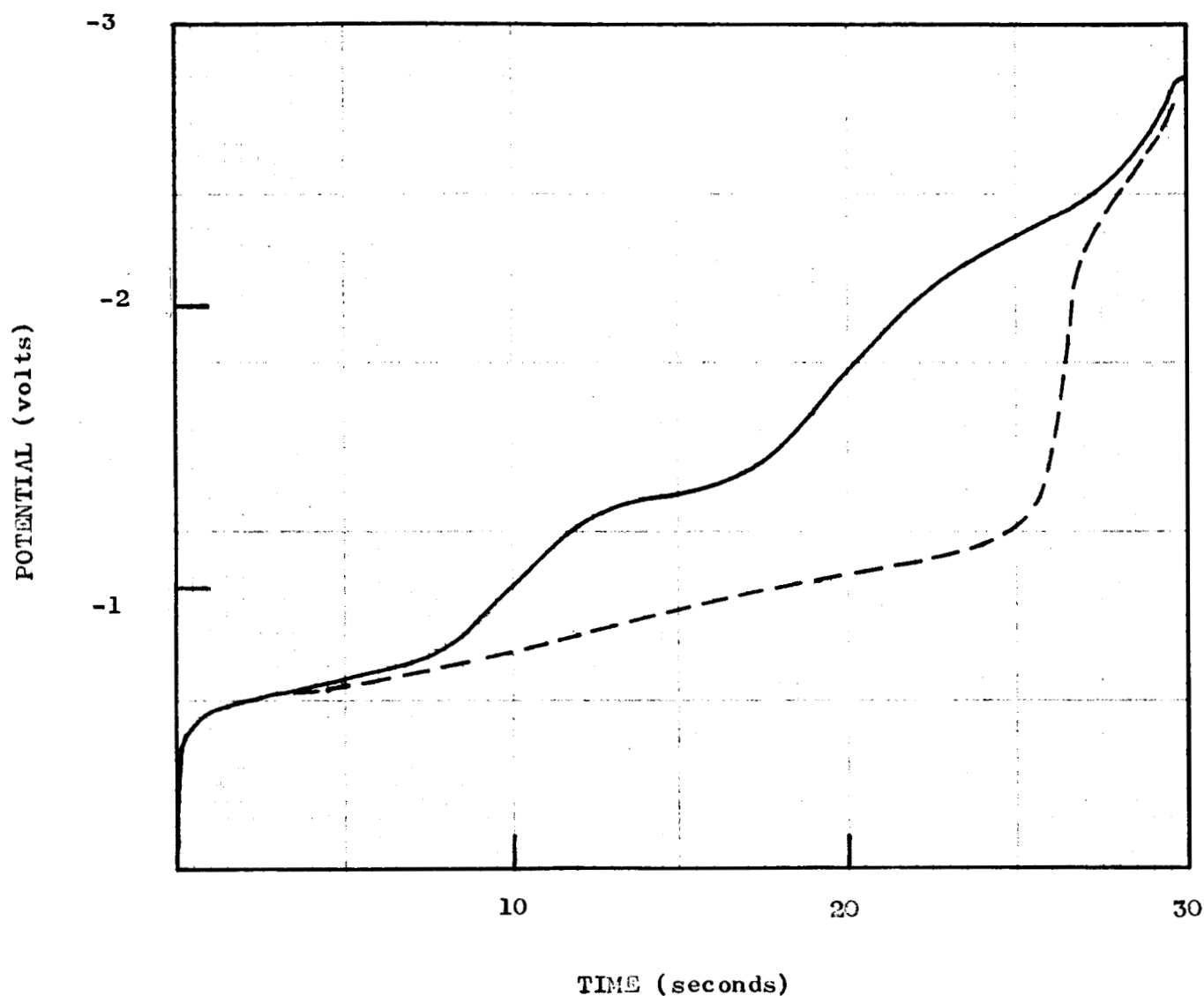


Figure 5: Cathodic chronopotentiograms showing the character of the reduction curve for species A, a deleterious impurity or group of impurities, which is always present in propylene carbonate solutions and is reduced at potentials more positive than the reduction potential for lithium. The solid-line chronopotentiogram was obtained in a solution, 1.0 M in LiClO_4 and 0.1 M in AlCl_3 at 1.5 mA cm^{-2} ; the dotted-line chronopotentiogram was obtained in a solution of 0.35 M in LiCl and 0.4 M in AlCl_3 at 2.0 mA cm^{-2} . The variations between the two chronopotentiograms probably reflect varying relative proportions of several constituent impurities which together comprise species A. Reproducible and well-defined chronopotentiograms have not been obtained in solutions from which AlCl_3 is absent.

An initial potential plateau at -2 V was observed followed by an approximately linear increase in potential to voltages greater than -5 V. It was not possible to obtain satisfactorily reproducible chronopotentiograms, values for $iT^{1/2}$ varying from 6.5 to 13 mA cm⁻² sec^{1/2}. Anodic recoveries were not obtainable; this, together with the observed linear increase in potential suggests that potassium is not reduceable to the metal but that reduction occurs in a fashion similar to that which prevails in lithium solutions containing water -- namely the production of a basic potassium salt at the electrode, such as K₂O or KOH. Chemical analysis of the violet deposits recovers an amount of base equivalent to the total current passed during deposition. No significant changes were observed when AlCl₃ was added to the solutions.

Solutions were prepared from equal volumes of 0.1 M KPF₆ and 0.1 M LiClO₄. A precipitate formed, doubtless KClO₄. Subsequent cathodic chronopotentiograms were similar to those obtained for lithium in LiClO₄ and in the mixed LiCl/AlCl₃ electrolytes, with $iT^{1/2} = 13.5$ mA cm⁻² sec^{1/2} for lithium deposition. Anodic efficiencies were low and further work on this electrolyte was discontinued.

5. Conclusions and future work on the lithium electrode. To date the most tenable hypothesis explaining the unsatisfactory anodic efficiency obtained with the lithium electrode is that, on cathodic reduction, lithium metal is co-deposited with lithium oxide or hydroxide -- a by-product of the decomposition of water or solvent. The cause of this may be inherent in the basic mechanism of reduction or may result from the presence of impurities. As yet satisfactory procedures for the clear detection and complete removal of impurities are not available. It is likely that improvement in the performance of the lithium electrode may be obtained with the addition of materials which scavenge water, most desirably through reduction to hydrogen, and it is possible that hydrides may serve this function. It is also likely that if the codeposition of lithium oxide or hydroxide results from the reduction of species coordinated to lithium which, on reduction, yield oxide or hydroxide ions, precipitating lithium salts at the electrode surface then improvement will attend the development of electrolytes which complex lithium more strongly than do other materials in solution and which are incapable of yielding lithium salts as a by-product of cathodic reduction. Further experiments will be conducted with particular interest in the possibility of developing electrolytes in which lithium may be complexed, and from which water may be chemically scavenged, and in the use of surface active materials.

IV. THE SILVER AND COPPER ELECTRODES

A. Summary of Previously Reported Work

Since the weight of active cathode material is significantly larger than that of anode material it is especially important that secondary battery cathodes should function efficiently. It was previously reported that both silver and copper may be oxidized to insoluble chloride salts in solutions containing a chloride donating material, such as AlCl_3 , and that AlCl_3 appears capable of donating all of its chlorides towards the formation of the salts. However, whereas the silver chloride is insoluble in propylene carbonate electrolytes the copper chloride is slowly soluble. The subsequent cathodic reduction of the insoluble salts formed on anodic oxidation is not clear-cut since possible concurrent reduction of impurities initially present as well as impurities produced as by-products during oxidation complicate the cathodic behavior.

B. Subsequent Observations and Conclusions

A major objective of this work is to modify the electrolyte in such a way as to decrease the solubility of the copper chloride formed on anodization. It is further desirable that electrolytes employing fluoride donating material be developed. In order to proceed systematically and logically with the modification of electrolytes reference electrodes meaningfully sensitive to the electrolyte composition must be developed. However, our investigations have been complicated by the fact that the electrolytes are unstable in that AlCl_3 is slowly lost. Therefore, much of our work during this quarter has been concentrated on investigating this phenomena and trying to eliminate its occurrence.

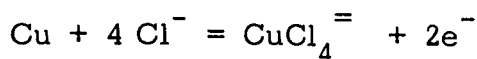
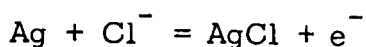
Initial investigations were conducted in propylene carbonate solutions of KPF_6 . In such solutions both copper and silver are oxidized to soluble ions rather than to insoluble salt deposits, and this is seen by the fact that if anodization is performed at moderate currents (e.g. 5 mA cm^{-2}) and, after a period of time, the current is reversed, the resultant cathodic chronopotentiogram will show a transition time equal to one-third the previous period of anodization.⁽⁴⁾ If the solution is stirred following

(4) P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers, Inc., New York, 1954, p. 195.

anodization, subsequent cathodization gives no potential break corresponding to the reduction of any previously formed anodic salt film. Thus insoluble salts of copper and silver and proved not to form in KPF_6 solution. If anodic chronopotentiograms are performed at sufficiently high currents an anodic transition time is observed when the potential sharply breaks from the plateau of +1 to +2 volts to +6 volts. Values for $iT^{1/2}$ of about $300 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ were obtained on copper in 0.2 M KPF_6 . We have no clear explanation for the cause of this potential break, but believe it due merely to charge depletion in the diffusion layer and not of immediate interest.

Following the electrochemical studies made in KPF_6 alone, similar experiments were performed following the addition of small increments of AlCl_3 to KPF_6 solutions until the final concentration was about 0.05 M in AlCl_3 . Anodic chronopotentiograms showed a potential break with an $iT^{1/2}$ approximately proportional to the concentration of AlCl_3 added, and subsequent cathodizations also gave a potential break when an amount of current had passed during cathodizations about equal to that previously passed during anodization. This is indicative of film formation but it was not possible to establish a more precise correlation between the concentration of AlCl_3 and anodic $iT^{1/2}$ because reproducibility was poor. Later experiments, described below, indicate that this lack of good reproducibility resulted from the failure to polish the electrodes after each run, and the failure to appreciate the slow, but constant loss of AlCl_3 from the solutions.

We then reverted to the use of LiClO_4 supporting electrolytes. It was found that anodic chronopotentiograms on polished cobalt electrodes gave a sharp potential break in 0.2 M LiClO_4 of about $250 \text{ mA cm}^{-2} \text{ sec}^{1/2}$; again we feel this represents charge depletion in the diffusion layer. The value for $iT^{1/2}$ should be compared with that of 300 obtained in KPF_6 solutions of equal concentration. A 0.2 M LiClO_4 solution was saturated with LiCl , 0.02 M , in order to see whether anodic behavior was significantly different from that observed when AlCl_3 served as the source of chloride. After stirring overnight well-defined anodic chronopotentiograms were obtained with a potential plateau at ca. +0.3 V followed by a potential break to ca. +1 V. The value for $iT^{1/2}$ was $5.1 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ on silver. It was necessary to polish the silver electrodes after each run to insure reproducibility. On copper $iT^{1/2}$ was only $2.6 \text{ mA cm}^{-2} \text{ sec}^{1/2}$. This suggests that the two reactions occurring respectively on silver and copper differ in the number of chlorides consumed per electron discharged as would be the case for the following reactions:



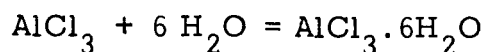
Further experiments were performed in which ml. increments of 1.0 M AlCl_3 were added. As expected, both the anodic and cathodic $iT^{1/2}$ increased, due respectively to the increased concentration of total chloride and the solubilization of lithium chloride by AlCl_3 . However, in the light of later experiments the values of $iT^{1/2}$ obtained are invalidated by the failure to appreciate the slow removal of AlCl_3 from solution with time.

A more concentrated LiClO_4 electrolyte, 0.4 M, was then employed. Anodic chronopotentiograms on silver were well-defined with an $iT^{1/2}$ of about $590 \text{ mA cm}^{-2} \text{ sec}^{1/2}$, twice that of the 0.2 M LiClO_4 and KPF_6 solutions. The solution was made 0.02 M in AlCl_3 and the anodic $iT^{1/2}$ determined for silver. In four hours $iT^{1/2}$ diminished from 10.0 to $5.2 \text{ mA cm}^{-2} \text{ sec}^{1/2}$, and after standing overnight had diminished to 1.3. An additional increment of AlCl_3 again increased $iT^{1/2}$ by the expected amount, but again the slow decrease with time was noted. It was assumed that if the decay in $iT^{1/2}$ was caused by the removal of AlCl_3 by residual water in the electrolyte, then complete removal of water should be marked by cessation of this decay of $iT^{1/2}$. This was not observed, even when the total concentration of AlCl_3 added was 0.1 M.

Similar solutions were then studied in which water was deliberately added. A solution, 0.4 M in LiClO_4 and 0.1 M in AlCl_3 , was prepared. It was noted that anodic chronopotentiograms were rather ill-defined in the more concentrated solutions but values of $55 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ were obtained. Incremental additions of water were made and the results are shown below:

<u>Concentration of water in moles liter⁻¹</u>	<u>Anodic $iT^{1/2}$ in mA $\text{cm}^{-2} \text{ sec}^{1/2}$</u>
0	55
0.05	48
0.10	43
0.15	39
0.25	27
0.30	23
0.35	18
0.40	11

It will be observed that the values of $iT^{1/2}$ extrapolate to 0 at about 0.6 M concentration of water. This agrees with the following reaction for removal of $AlCl_3$:

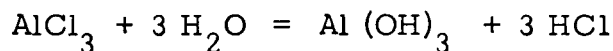


The linearity of the decrease in $iT^{1/2}$ with increasing concentration of water is also important in suggesting that intermediate species such as $AlCl_2(H_2O)^+$ are never present in significant concentrations.

A similar series of experiments were performed with a lower initial concentration of $AlCl_3$. Anodic chronopotentiograms were made on silver in a solution, 0.4 M in $LiClO_4$ and 0.04 M in $AlCl_3$. More sharply defined transition times were obtainable at these lower concentrations, and reproducibility was improved by reducing the silver chloride film after each run potentiostatically at -0.2 V. Again the incremental decrease in $iT^{1/2}$ following the incremental addition of water corresponded to the above reaction.

A series of experiments were performed in which to solutions, 0.5 M in KPF_6 , were added varying amounts of water. To each of these "wet" solutions was then added enough $AlCl_3$ to make the solution initially 0.046 M. The anodic $iT^{1/2}$ was measured at various periods of time following the initial addition of $AlCl_3$. The results are shown in Figure 6.

The solution to which water had not been added was allowed to stand overnight and the argon which was passed through a tube containing P_2O_5 and thence over the solution was removed through a solution of standard alkali, the base collector solution. After overnight standing it was found that $iT^{1/2}$ had decreased to negligible values and that the amount of base which had been consumed was exactly three times the number of millimoles of $AlCl_3$ initially added. Further chemical analyses indicated that consumption of base resulted from the removal of HCl from the electrolyte, indicating the following reaction to have occurred:



The initial reaction involving the precipitation of $AlCl_3 \cdot 6H_2O$ is then followed by the slower evolution of gaseous HCl .

In another experiment a solution, 0.5 M in KPF_6 and 0.046 M in $AlCl_3$, was again investigated but water was not added. During this experiment the rate at which HCl was evolved was followed by titrating aliquots of the base collector solution. The results are shown in Figure 7.

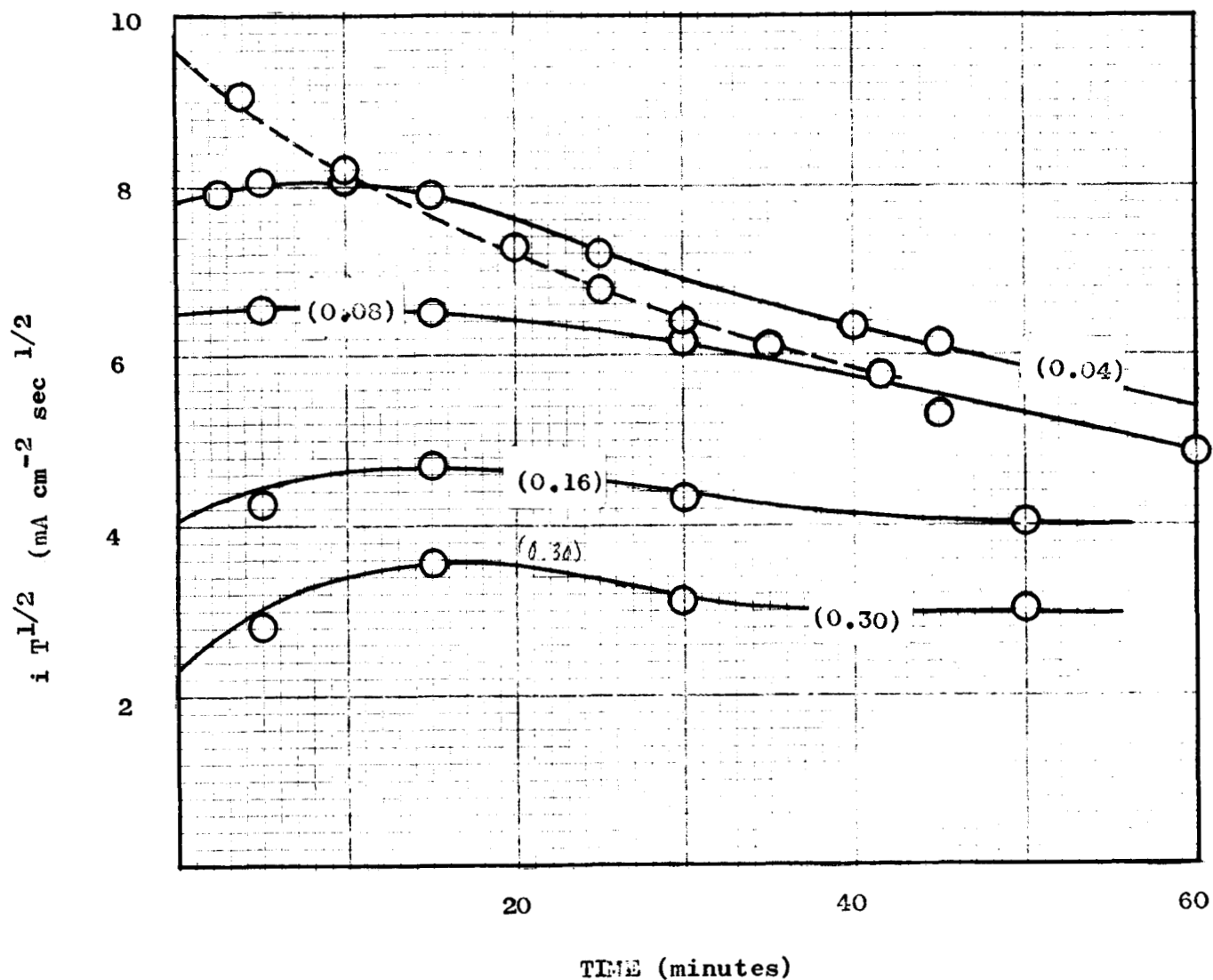


Figure 6: Decrease in anodic chronopotentiometric $i T^{1/2}$ for AlCl_3 with time. Values for $i T^{1/2}$ obtained on polished silver electrodes and reflect the process: $3 \text{Ag}^+ + \text{AlCl}_3 = 3 \text{AgCl} + \text{Al}^{+3}$. The decrease in $i T^{1/2}$ reflects the slow loss of AlCl_3 from solution. Runs were performed on separate solutions, each initially 0.5 M in KPF_6 and 0.046 M in AlCl_3 . Before the addition of aluminum to the solution, water was added to give the concentration shown in parentheses by each curve. The dotted line curve represents the solution to which water was not added.

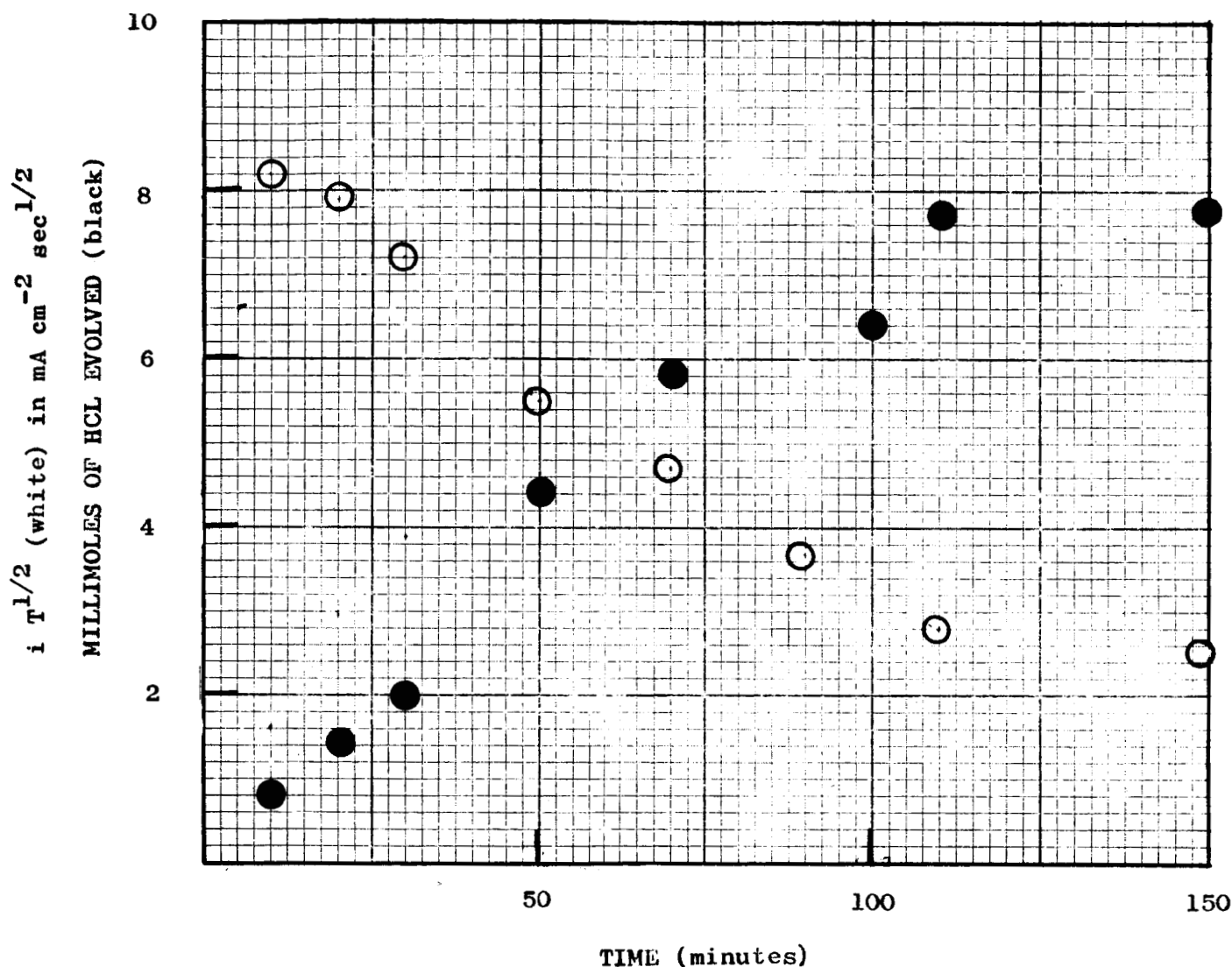


Figure 7: Relationship between decrease in $i T^{1/2}$ for AlCl_3 with evolution of HCl . Solution was initially 0.5 M in KPF_6 and 0.046 M in AlCl_3 . Anodic chronopotentiograms performed on silver, and decrease in $i T^{1/2}$ reflects removal of AlCl_3 from solution. The evolved HCl was collected in standard base and the amount of HCl evolved was determined by titrating aliquots of the base collector solution with standard acid.

Two further experiments were performed in which no supporting electrolyte was present. In the first experiment a 0.05 M solution of AlCl_3 alone was allowed to stand with deaeration overnight. Back titration of the basic collecting solution with standard acid indicated that little HCl had been evolved. In the second experiment a 0.05 M solution of AlCl_3 was made, 0.02 M in H_2O . The rate at which HCl was evolved was measured by titrating aliquots of the base collector solution. It was found that the initial evolution was rapid and that the amount of HCl passed over within the first 20 minutes was close to the amount of water initially added. Thereafter the rate at which HCl was evolved was much slower. The results are shown in Figure 8.

It seemed likely that the removal of AlCl_3 through reaction with water would proceed more slowly in the presence of a supporting electrolyte which has a greater affinity for water than does KPF_6 - solutions of $\text{Mg}(\text{ClO}_4)_2$ were used for this purpose. A solution, 0.25 M in $\text{Mg}(\text{ClO}_4)_2$, was made 0.05 M in AlCl_3 , and an anodic $iT^{1/2}$ of $20.4 \text{ mA cm}^{-2} \text{ sec}^{1/2}$ was found. The solution was then made 0.06 M in water which should, by the reaction: $\text{AlCl}_3 + 6 \text{H}_2\text{O} = \text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ decrease the concentration of AlCl_3 to 0.04 M, 80% of the initial value, whereupon $iT^{1/2}$ was found to have decreased to 19.0. After standing overnight, $iT^{1/2}$ had decreased to $6.7 \text{ mA cm}^{-2} \text{ sec}^{1/2}$, only 1/3 the initial value. However, the amount of HCl which had been evolved was only slightly larger than the equivalent amount of water initially added.

A second experiment was performed with a solution of identical composition to that used in the preceding experiment except water was not added. In this experiment $iT^{1/2}$ decreased to 1/2 its initial value after overnight deaeration. However, the amount of HCl which had evolved from the solution was almost the same as had been evolved when water had been deliberately added.

The effect of water in removing AlCl_3 was investigated through a final series of experiments in which varying amounts of water were added to solutions initially 0.081 M in AlCl_3 . Upon the addition of water a precipitate formed. The solution and suspended precipitate were allowed to equilibrate in stoppered vessels overnight after which they were centrifuged and, after pouring off the supernatant liquid, the precipitates were analyzed for chloride and aluminum. The results are shown in Figure 9. Subtracting the maximum amount of precipitate obtained from the initial concentration of AlCl_3 indicates that $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is soluble to the extent of about 0.01 to 0.02 M. It will be noted that the precipitate is completely soluble when about eighteen moles of water have been added per

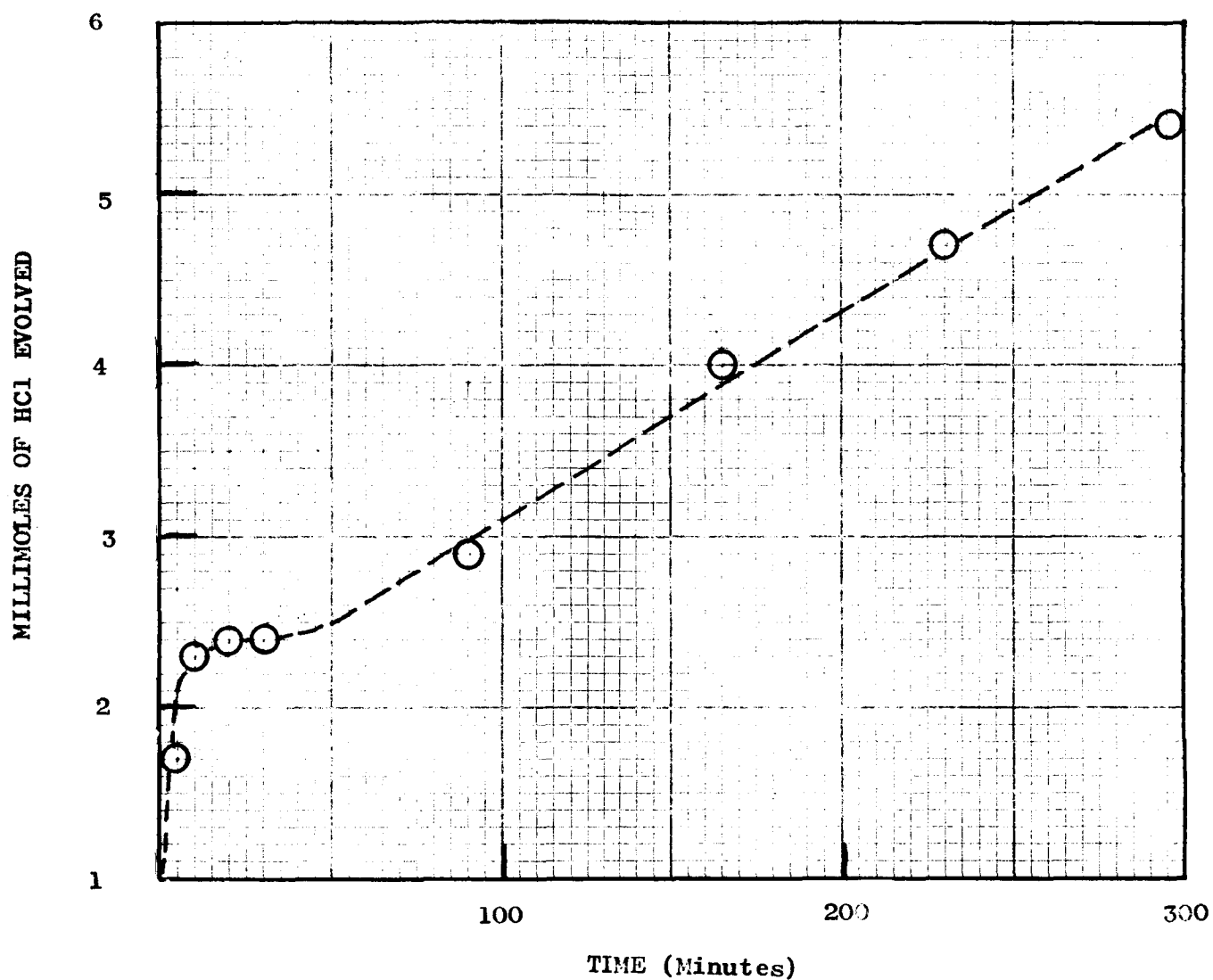


Figure 8: Rate of evolution of HCl from an AlCl_3 solution containing water. To 100 ml. of 0.05 M AlCl_3 was added enough water to make the solution initially 0.02 M in H_2O -- a total of 2 millimoles. The evolved HCl was collected in standard base and the amount of HCl evolved was determined by titrating aliquots of the base collector solution with standard acid.

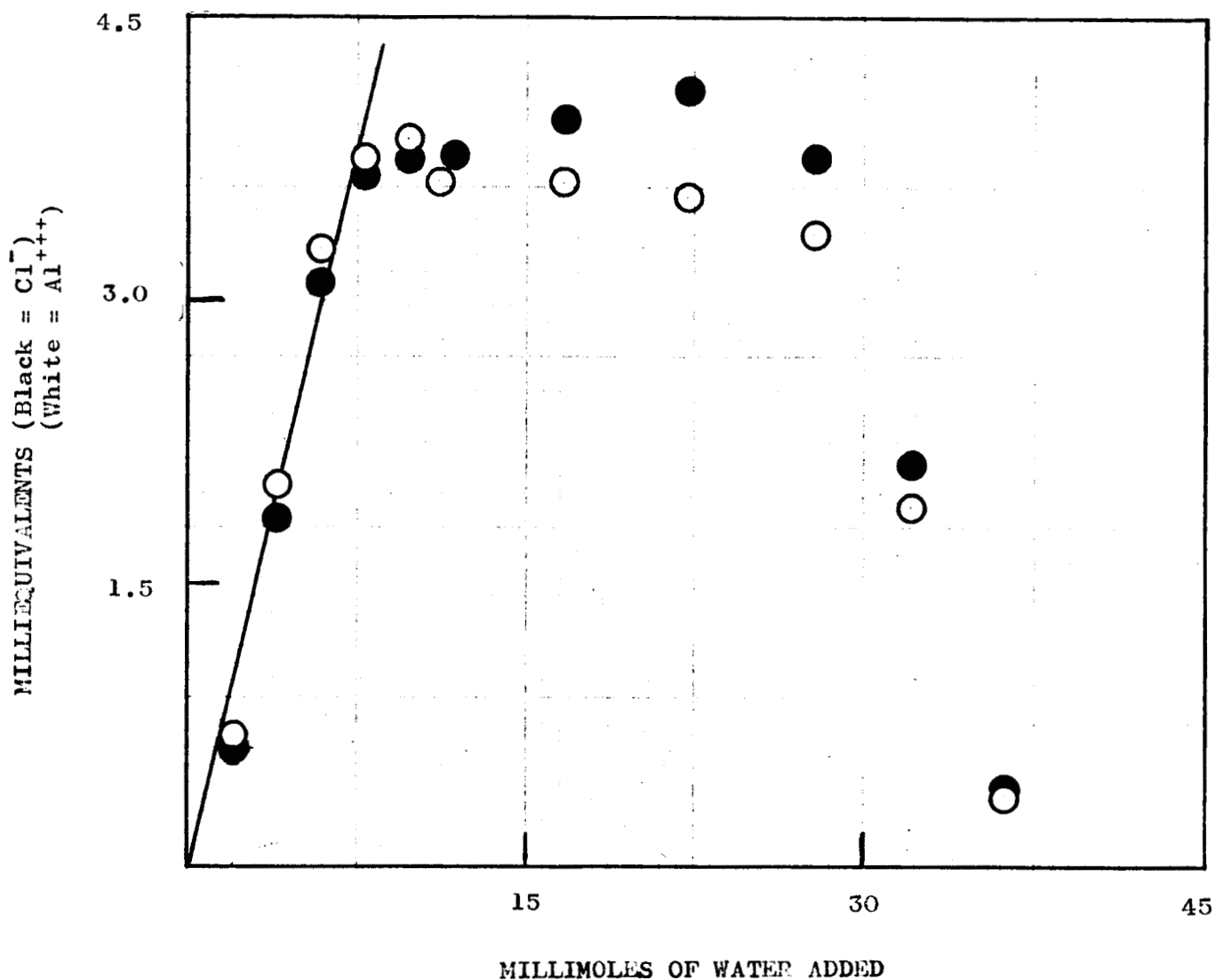
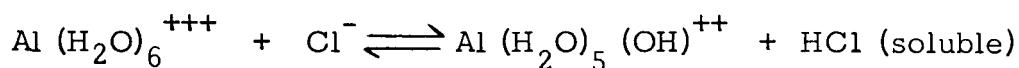
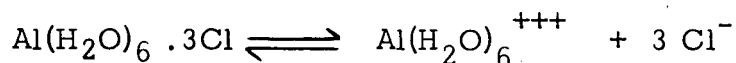


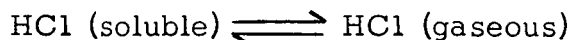
Figure 9: Chemical analysis of precipitate formed when water is added to 0.081 M AlCl_3 in propylene carbonate. To 20 ml. of solution were added amounts of water indicated in the figure. After overnight equilibration in sealed vessels, the solutions were centrifuged, and after discarding the supernatant liquid the precipitates were dissolved in water and analyzed for chloride and aluminum. Results of analyses are given in milliequivalents; one millimole of chloride ion = one milliequivalent; one millimole of aluminum ion = three milliequivalents.

mole of AlCl_3 , corresponding to the reaction: $\text{AlCl}_3 + 18 \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_6^{+++} + 3 \text{Cl}(\text{H}_2\text{O})_4^-$. Preliminary experiments indicate that larger amounts of water than this are required to solubilize $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of supporting electrolyte, probably because the complexation of species such as Li^+ and Mg^{++} with water is stronger than that of chloride.

It seems clear that there are a number of alternative processes by which AlCl_3 is removed from solution. One process is rapid which involves the immediate precipitation of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and most likely results from the displacement of chloride by water to give the hydrated aluminum ion, following which precipitation of the chloride salt occurs. The second process is much slower and may reflect an equilibrium situation such as the following:



and



It must again be emphasized that the primary purpose of these studies concerning the effect of water is to learn something about the nature of the basic chemical processes and the equilibria peculiar to these electrolyte systems. Water is a Lewis base, and the addition of water to non-aqueous solutions of Lewis acids is analogous to the titration of aqueous acid with aqueous base. Our concern with such questions arises from the fact that electrode behavior is not easily interpretable in the absence of such elementary information, and logical and systematic procedures for the improvement of electrode performance through electrolyte modification is not possible without such information.

We have commenced a series of experiments directed toward the development of suitable reference electrodes which meaningfully reflect electrolyte properties. It has been found that the potential of a silver electrode in propylene carbonate solutions of AgClO_4 containing excess supporting electrolyte obeys the Nernst expression, the potential increasing with the term, $0.059 \log [\text{AgClO}_4]$. Such an electrode functions as a satisfactory reference electrode. More work is planned on the development of suitable nonaqueous reference electrodes of silver.

The potential of a silver electrode covered with a film of silver chloride is well-poised and reversible. The titration of solutions of AlCl_3 with water, AgClO_4 , and LiCl , and electroformed Cu^+ and/or Cu^{++} will be performed in a further attempt to learn more about the equilibria extant in this electrolyte.

V. THE BERYLLIUM COMPLEX SALT ELECTROLYTES

The complex salt of beryllium chloride and diethylberyllium was prepared in 0.25 molar quantities and diluted with an equal volume of tetrahydrofuran. The resulting clear yellow solution, which had a specific conductivity of $7 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$, was investigated for its electrochemical properties in the usual manner, using copper working electrodes and a silver reference electrode. Metallic appearing beryllium deposits could be obtained at all current densities studied, however, in thick layers these deposits become black and amorphous looking. They could be completely removed by reverse current. No cathodic transition time could be obtained within the capabilities of the equipment used. Anodic stripping studies were carried out over the current range of 0.01 to 1.0 ma. and up to 100 millicoulombs of deposit with the following results:

- a. Anodic efficiency decreases slightly with increasing number of millicoulombs.
- b. Anodic efficiency increases with increasing anodic current density.
- c. Anodic efficiency decreases with increasing cathodic current density.
- d. The efficiency averages 85 to 90% at 10 to 100 millicoulombs and approaches 100% below 10 millicoulombs.

Anodization experiments gave brownish-black films of copper chloride which were non-adherent and electrochemically inactive. Close examination of the electrode surface revealed that a yellow layer of dissolved chlorine is initially formed which then reacts chemically with the copper to give the black solid product.

Attempts to determine the cathodic efficiency by deposition, dissolution, and back-titration gave erratic results. A run at 8 ma/cm^2 for 3 hours gave 50% efficiency while a run at 0.4 ma/cm^2 for 5 1/2 hours gave 200% efficiency. Causes for the discrepancy have not yet been determined.

In order to determine whether the beryllium was deposited from species provided by the beryllium chloride or the diethylberyllium, a second complex salt was prepared from tetraethylammonium chloride and diethylberyllium diluted with tetrahydrofuran. No beryllium could be deposited from this solution under any conditions, indicating that either BeCl^+ or

Be^{++} is responsible for the results in beryllium chloride containing solutions.

As an outgrowth of the successful deposition and dissolution of beryllium from beryllium chloride-diethylberyllium complex, a variety of relevant cell systems was examined for beryllium deposition.

Anhydrous beryllium chloride was added to a tetraethylammonium chloride-diethyl-beryllium complex. It was thought that perhaps the tetraethylammonium chloride might act as a supporting electrolyte of high conductivity. No beryllium deposit could be obtained from this system.

Beryllium chloride tetrahydrofuranate was dissolved in anhydrous ethylenediamine. It dissolved slowly with minor heat evolution. In this approach it was considered that the ethylenediamine might coordinate with the beryllium ion sufficiently to promote ionization of the beryllium chloride molecule. Although good conductivity was observed - low IR drop - no beryllium metal deposit could be obtained.

Beryllium chloride tetrahydrofuranate was dissolved in 0.5 M aluminum chloride-propylene carbonate solution. Although solubility and conductivity were quite good, nothing was obtained on cathodization that could be identified with certainty as beryllium. Cathodic waves were complex and difficult to reproduce. An anodic transition time was obtained along with a black chloride film on the copper electrode.

Freshly prepared beryllium chloride tetrahydrofuranate and diethylberyllium diluted with tetrahydrofuran were used to prepared the complex which was placed in the main compartment of the electrolysis vessel. The side compartment, separated by a fritted disc, was filled with a lithium chloride, aluminum chloride, propylene carbonate solution. Lithium was deposited on a platinum electrode, beryllium on a copper electrode and the potentials measured with respect to each other and a silver reference electrode in the main compartment. A very large IR drop existed between the two compartments as indicated by the average lithium-silver potential of -1.6 volts. The average beryllium-silver potential was -0.6 volts and the lithium-beryllium potential was -0.9 volts. Since the usual lithium-silver potential is -3.0 volts, it can be roughly estimated that the lithium-beryllium potential in the absence of significant IR and liquid junction effects should be about -2.4 volts. After standing overnight the solution no longer gave beryllium deposits or chloride films on copper nor did the addition of fresh beryllium chloride regenerate the system. Further investigations are planned to improve the reproducibility of the reversible beryllium system.

VI. CONCLUSIONS AND FUTURE WORK

At this point we feel that the failure of the lithium electrode to operate with satisfactory efficiency is not due to the presence of small amounts of impurities but rather to the fundamental nature of the cathodic reaction in propylene carbonate. A more detailed investigation of this reaction is limited by the fact that depositions cannot be studied at very low current densities since such currents result only in the reduction of impurities. We shall continue in our attempts to remove the last vestiges of these impurities primarily through electrolytic pre-treatment and possibly through the addition of appropriate chemical scavengers.

The development of satisfactorily reversible cathodes is primarily a problem in the development of electrolytes in which the salt films formed on charge are sufficiently insoluble. We shall continue our work in attempting to determine the nature of the species, reactions, and equilibria extant in these electrolytes, augmenting the information obtained to date with potentiometric data. We shall begin a study of the behavior of electrodes prepared by anodically forming oxide, chloride, and fluoride salts of manganese, cobalt, iron, nickel, copper, and silver in appropriate aqueous media, and will be concerned with the cycling characteristics of such electrodes in propylene carbonate electrolytes.